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REPORT SD-TR-88-27

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Perfluoropolyalkylether Lubricants under Boundary Conditions:
Iron Catalysis of Lubricant Degradation

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1 March 1988

Prepared for
SPACE DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Base
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This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-85-C-0086-P00016 with the Space Division, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009-2960. It was reviewed and approved for The Aerospace Corporation by M. J. Daugherty, Director, Electronics Research Laboratory.

Capt. Buford W. Shipley, CWDE, was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) Program.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

A193 241

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS			
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT			
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		Approved for public release; <u>distribution unlimited</u>			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) TR-0086A(2945-03)-6 ✓		5. MONITORING ORGANIZATION REPORT NUMBER(S) SD-TR-88-27 ✓			
6a. NAME OF PERFORMING ORGANIZATION The Aerospace Corporation Laboratory Operations	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Space Division Los Angeles Air Force Base			
6c. ADDRESS (City, State, and ZIP Code) El Segundo, CA 90245		7b. ADDRESS (City, State, and ZIP Code) Los Angeles, CA 90009-2960			
8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F04701-85-C-0086-P00016			
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)

Perfluoropolyalkylether Lubricants Under Boundary Conditions:
Iron Catalysis of Lubricant Degradation12. PERSONAL AUTHOR(S)
David J. Carre

13a. TYPE OF REPORT	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) 1988 March 1	15 PAGE COUNT 22
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16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	HPLC	Lubricant degradation	SAM
			IR/spectroscopy	Lubricants	SIMS
			Lewis acids	Perfluoropolyalkylether (PFPE) oils	XPS

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Perfluoropolyalkylether (PFPE) oils and oil-based greases exhibit significant degradation under boundary lubrication conditions. In the absence of significant concentrations of oxygen, as in the case of spacecraft orbital environments, the degradation mechanism consists of two steps: (1) the initial reaction of the PFPE molecules with freshly exposed iron to form the Lewis acid, FeF_3 , followed by (2) the reaction of the FeF_3 with unreacted PFPE molecules, which results in the cleavage of the etherate linkages. The result is an autocatalytic degradation that takes place at temperatures below the onset of thermal decomposition. This mechanistic hypothesis is supported by the following experimental results: (1) The reaction of PFPE with FeF_3 has been shown to give rise to fluorinated-ketone and acid fluoride ether-cleavage products that are more reactive than the parent PFPE molecules and have lower molecular weights and thus poorer lubricating ability. (2) FeF_x compounds are formed in the wear tracks of wear-test components under boundary lubrication conditions. On the basis of these experimental results, poor performance can be predicted for PFPE oils.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

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SECURITY CLASSIFICATION OF THIS PAGE

under conditions in which high temperatures ($\approx 350^{\circ}\text{C}$) and freshly exposed metal surfaces are present (i.e., the conditions of boundary lubrication). This prediction is corroborated through wear tests in which the performance of PFPE is compared to the performances of commercial petroleum-based and synthetic-hydrocarbon lubricants to which lead naphthenate or antimony dialkyldithiocarbamate has been added. The test results confirm the well-known fact that the antiwear additives are very important to prolonged wear life under boundary lubrication conditions. In addition, the results show that, compared to the other lubricants tested, the PFPE lubricants do not demonstrate adequate lubrication performance. Both the PFPE degradation mechanism and the fact that soluble antiwear additives are not currently available imply that PFPE lubricants are not suitable for applications in which boundary lubrication conditions exist, especially when high loads are involved.

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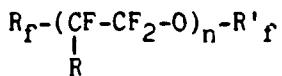
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I. INTRODUCTION

Perfluoropolyalkylether (PFPE) oils and oil-based greases have become popular since their development for spacecraft applications. Their increasing use results from their favorable properties, which include a wide-application temperature range, low vapor pressure, a good viscosity index, and general chemical inertness. The chemical inertness of these materials, however, must be evaluated in the light of extended satellite-mission lifetimes and the rigors of operation in the orbital environment. These PFPE materials can be described by the general formula



where R_f and R'_f are perfluoropolyalkylether end groups of unspecified length, R is F or CF_3 , and n is approximately 20.

Under boundary lubrication conditions, conventional hydrocarbon lubricants rely on antiwear additives to minimize the effects of metal-to-metal interaction and to extend the performance of lubricants. Unfortunately, the PFPE fluids, because of their chemical composition, exhibit very limited solvent power and will dissolve very few materials. Since soluble antiwear additives are desirable, there have been recent attempts to synthesize soluble additives for PFPE oils, but to date, with the exception of anti-oxidants having limited thermal stability,¹ little success has been achieved. Thus, under boundary conditions in vacuum, in the absence of additives, PFPE reacts with the metal surfaces, causing the lubricant to degrade and thus limiting its performance.

PFPE oils, although relatively unreactive, have been shown in laboratory experiments to react under certain conditions. Reaction with iron and titanium alloys at elevated temperatures ($>260^\circ C$) under oxidizing conditions causes the metals to corrode and degrades the PFPE.^{2,3} At moderate temperatures ($\approx 170^\circ C$), perfluorinated ethers have been shown to react with Lewis acids,

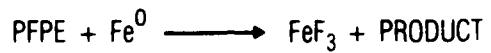
such as AlCl_3 ; these Lewis acids in turn cause the etherate linkages to cleave and fluorinated ketone and acid fluoride degradation products to form.^{4,5,6}

In our laboratories a PFPE oil-based grease was used as one of the lubricants in a series of ball-bearing tests designed to study lift-off phenomena. Following testing, the bearings were disassembled and examined. Underneath a layer of fluorocarbon-polymer thickener that had been burnished on the raceways, the raceway surfaces were extensively pitted, indicating that the system had degraded chemically and physically. Auger analysis of the raceway surfaces indicated that fluorine was present. Clearly, since the bearings were run in a vacuum chamber at very low pressure and thus at a very low oxygen partial pressure, nonoxidative degradation of the grease must have occurred.

On the basis of these observations, we proposed a mechanism to explain PFPE degradation at very low oxygen partial pressure, i.e., in the spacecraft orbital environment. The steps in the proposed mechanism are (1) the interaction between fluorocarbon and steel surfaces to form FeF_3 , followed by (2) the degradation of the PFPE oil through the FeF_3 -mediated cleavage of the etherate linkages (see Fig. 1). This hypothesis was supported by several studies reported in the literature. The reaction between fluorocarbon and iron metal leading to dehalogenation of the fluorocarbon has been observed in systems in which aromatic products were formed,⁷ but has not been reported for aliphatic systems. (The formation of the incipient aromatic transition state and products undoubtedly contributes to a lowering of the reaction energy barrier and facilitates the reaction.) The possible formation of FeF_3 in these reactions was not reported, although such formation was likely. The formation of metal-fluoride compounds has been inferred from the reactions of PFPE oil with aluminum and iron alloys under oxygen-containing atmospheres⁸ and titanium under oxygen and nitrogen.⁹

In order to prove the validity of the hypothesized mechanism whereby PFPE degrades under boundary conditions and orbital environments, studies were undertaken in our laboratory to demonstrate the following: (1) that FeF_3 forms on stainless-steel surfaces through the reaction of PFPE with iron;

STEP 1:



STEP 2:

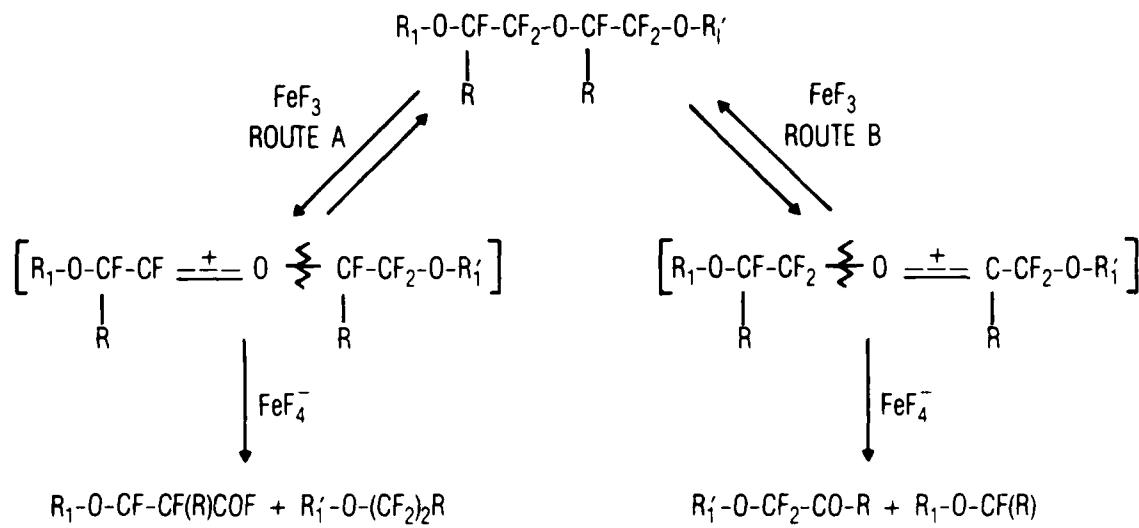


Fig. 1. Scheme for the Degradation of PFPE at Very Low Oxygen Partial Pressure

(2) that FeF_3 reacts with PFPE to result in etherate-linkage cleavage at temperatures below the onset of thermal degradation; and (3) that because of the aforementioned degradation mechanism, the PFPE fluids do not perform well under boundary conditions.

This paper constitutes a review of this work and its implication regarding the performance of PFPE lubricants in tribological systems. Although a more detailed account of the results and experimental procedures is given elsewhere,¹⁰⁻¹² some experimental information will be given in the following section to help the reader understand the nature of the experimental study.

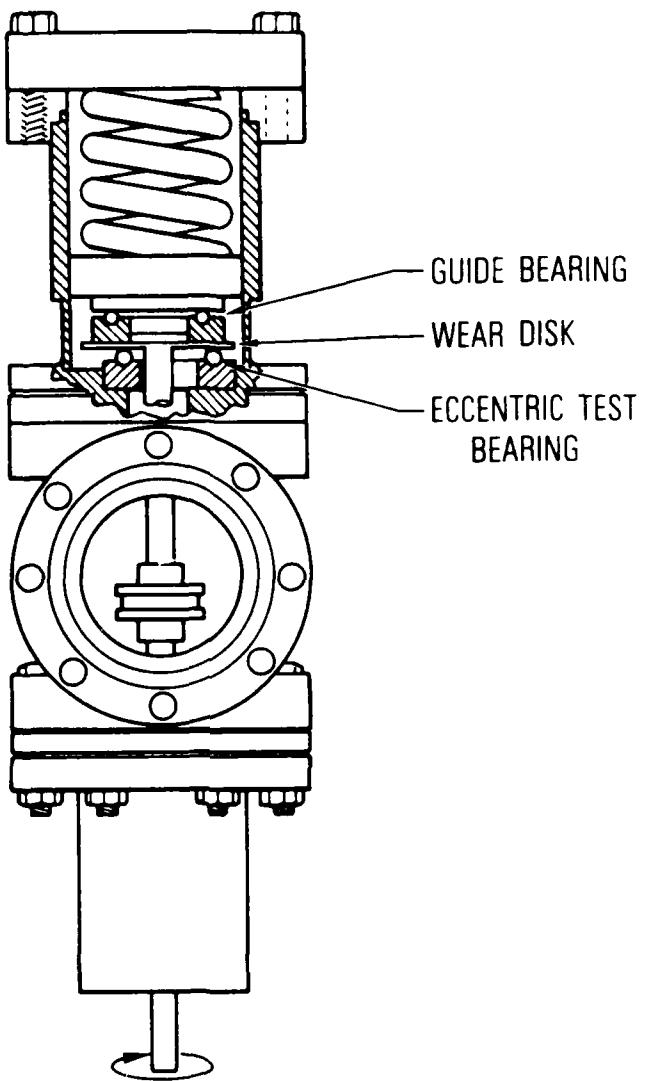
II. RESULTS AND DISCUSSION

A. FORMATION OF FeF₃ ON STEEL SURFACES

In order to demonstrate that FeF₃ forms on stainless-steel surfaces through the reaction of PFPE with iron, it was necessary to operate under boundary lubrication conditions. These conditions result in the generation of high temperatures in the asperity contact region and in the continuous exposure of the fresh metal surfaces that are required for the hypothesized reaction to proceed. In order to achieve the required conditions, an apparatus was designed and fabricated to operate in the boundary lubrication regime and yield samples that are amenable to analysis by surface spectroscopic techniques.

The apparatus uses a thrust bearing-on-disk arrangement, with the axes of rotation of the two interacting members not coaxial but eccentric by $\approx 2 \text{ mm}$ ¹⁰ (see Fig. 2). This eccentricity results in a slide-to-roll ratio of 0.16 and thus creates boundary conditions, even at high speeds. The lubricant samples (sample size = 25 microliters) were run at 1750 rpm, with 10 lb (44.5 N) of applied axial load under a pressure of $\approx 1 \times 10^{-7} \text{ Torr}$ ($1.3 \times 10^{-5} \text{ Pa}$). (The 10-lb applied load resulted in a calculated Hertzian stress of $\approx 115,000 \text{ psi}$ ($7.9 \times 10^8 \text{ Pa}$) in the contact region.¹³) So that the fluoride-containing species on the surfaces could be observed, the runs were stopped after 48 hr, well short of failure.

The surface analyses were performed after the disk surfaces were cleaned. The wear disks were washed in solvent to remove residual lubricant, then were heated to $\approx 400^\circ\text{C}$ to pyrolyze fluorocarbon polymer that had been burnished on the disk surfaces. (Analyses of disks coated with fluorocarbons, but not run in the wear-test apparatus, showed that the fluorocarbons did not react with the iron surfaces at the pyrolysis temperature.) After the disks were cleaned, their surfaces were analyzed by x-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and Auger electron spectroscopy (AES).



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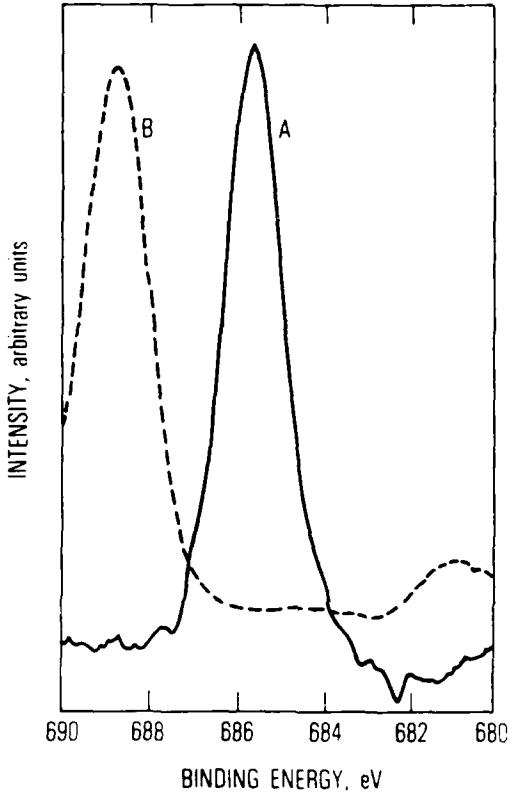
Fig. 2. Eccentric Thrust Bearing-on-Disk Wear Test Apparatus

The results of the XPS analyses showed that fluoride ions were definitely on the disk surfaces (Fig. 3), and the AES analysis indicated that fluoride ions were limited to the wear-track on the disk surface (Fig. 4). (The XPS peaks for iron were not intense enough to be used to determine the iron oxidation state.)

The nature of the surface fluoride compounds was revealed, to a degree, in the SIMS data. In addition to the stainless-steel constituents -- iron, chromium, and nickel -- in the wear track and typical background signals, strong signals at $m/e = 75$ and 19 , corresponding to FeF^+ and F^+ , respectively, were observed. The presence of these ions indicates that iron-fluorine compounds were in the wear track. Because both FeF_2 and FeF_3 give rise to these ions in SIMS analysis, we could not distinguish between the two possibilities. However, the presence of both fluoride ions and oxidized iron on the surface implies that oxidation-reduction reactions were taking place. In addition, the oxidation potential of fluorine is sufficient to have oxidized Fe^0 and Fe^{+2} to Fe^{+3} (Ref. 14). Thus, it is reasonable to assume that the iron in the wear-track areas on the disk surfaces was in the +3 oxidation state.

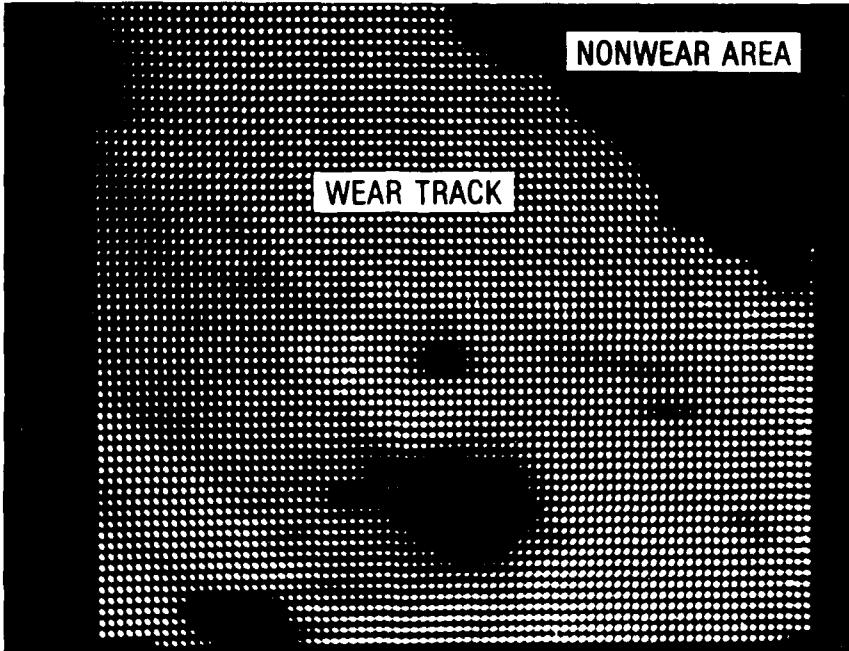
B. REACTION OF PFPE WITH LEWIS ACIDS

The reactions of a branched PFPE oil with FeF_3 , AlF_3 , and AlCl_3 were studied in an inert (nitrogen) atmosphere at high temperatures. The conditions necessitated the use of an autoclave system having a nonreactive nickel insert. (PFPE fluids do not react significantly with nickel at the temperatures used in this study.¹⁵) At the end of a run, the products were analyzed by means of infrared (IR) spectroscopy and high-performance liquid chromatography (HPLC) in the gel-permeation chromatography (GPC) mode. The IR results (Fig. 5) indicate that fluorinated carbonyl compounds, fluorinated ketone (with an absorption band at 1806 cm^{-1}) and acid fluoride (with a doublet at 1878 and 1886 cm^{-1}), were formed at 350°C , which is consistent with the mechanism shown in Fig. 1. The reaction temperature of 350°C is $\approx 25^\circ\text{C}$ below the temperature at which thermal degradation becomes significant. The minimum temperature at which thermal decomposition is important was determined in a



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Fig. 3. XPS Spectra at the Fluorine Binding Energy: (a) Fluoride Ion in the Wear Track, (b) Covalent Fluorine



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Fig. 4. AES Fluorine Elemental Map of Wear Disk Surface.
Signal intensity is proportional to surface
concentration of fluorine.

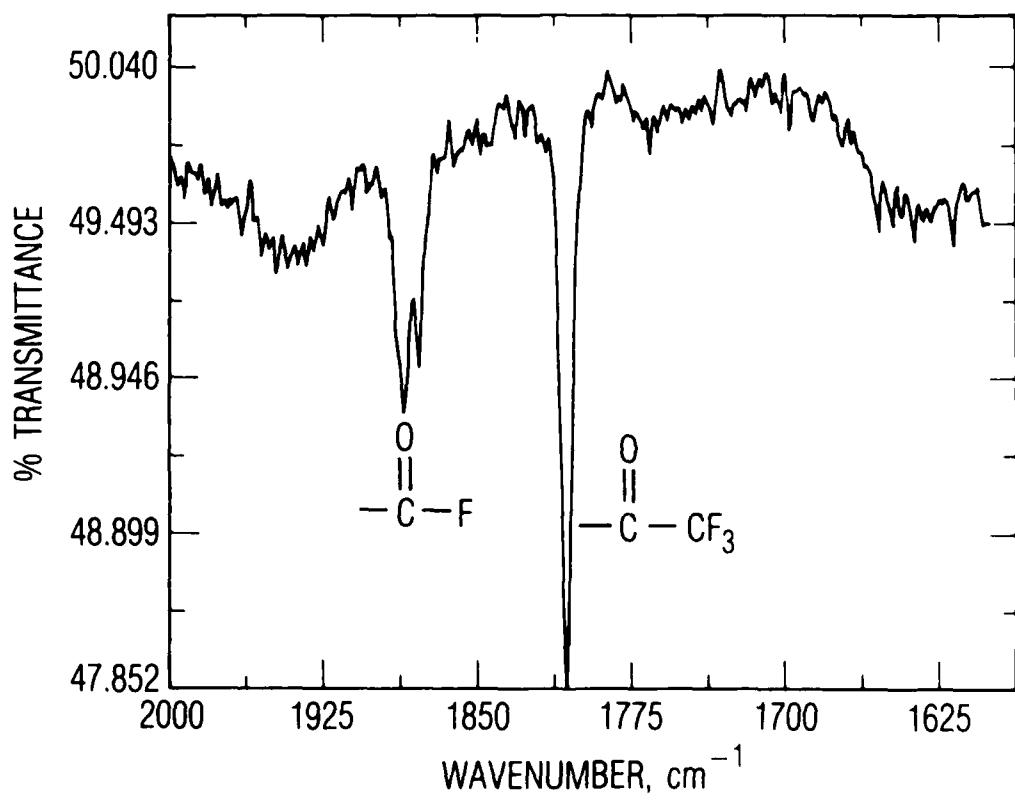


Fig. 5. IR Spectrum of the Products of FeF_3 -Catalyzed Degradation of PFPE Oil

separate experiment that used the same apparatus; this temperature is consistent with minimum estimates of the temperatures present at asperity contacts under boundary conditions.^{16,17} The HPLC-GPC data showed that the cleavage reaction is accompanied by a reduction in the molecular weight of the products, which is also consistent with the proposed mechanism.¹¹

C. PFPE PERFORMANCE UNDER BOUNDARY CONDITIONS

The performance of PFPE oils and greases under boundary lubrication conditions was assessed by means of the wear-test apparatus discussed above. Two sets of wear tests were performed. In the first set, the performance of a branched PFPE oil was compared with that of several commercially available synthetic hydrocarbon and petroleum-based oils containing antiwear additives. In the second set, the performance of a linear PFPE oil-based grease was compared to that of the same grease intentionally contaminated by a hydrocarbon oil with additives. (It has been suggested that the performance of PFPE oils under boundary conditions was improved by the presence of a small amount of hydrocarbon contamination.^{10,18}) Test failure was arbitrarily chosen to be a 50% increase in running torque.

The results of the first test series, shown in Fig. 6, are plotted as a series of parallel lines. (The data are plotted in this fashion because of some unique characteristics of the fixture. As the alignment of the wear members is not entirely reproducible, slight variations in the actual Hertzian stress levels occur in the contact region. These are manifested as facility-induced differences in running torque that contribute to the observed wear lives of the sample. These effects can be normalized by plotting the wear life as a function of observed torque.) The lubricants with the longest wear lives and lowest running torques, which appear in the upper left-hand portion of the figure, exhibit the best performance under the test conditions.

It is obvious from an examination of these data that the synthetic oils outperformed both the PFPE oils and petroleum-based oils. (The preparation and characteristics of the synthetic oils undoubtedly lead to improved properties. However, a discussion of the virtues of synthetic-hydrocarbon lubricants is beyond the scope of this paper.) Regarding the mechanism of PFPE degradation,

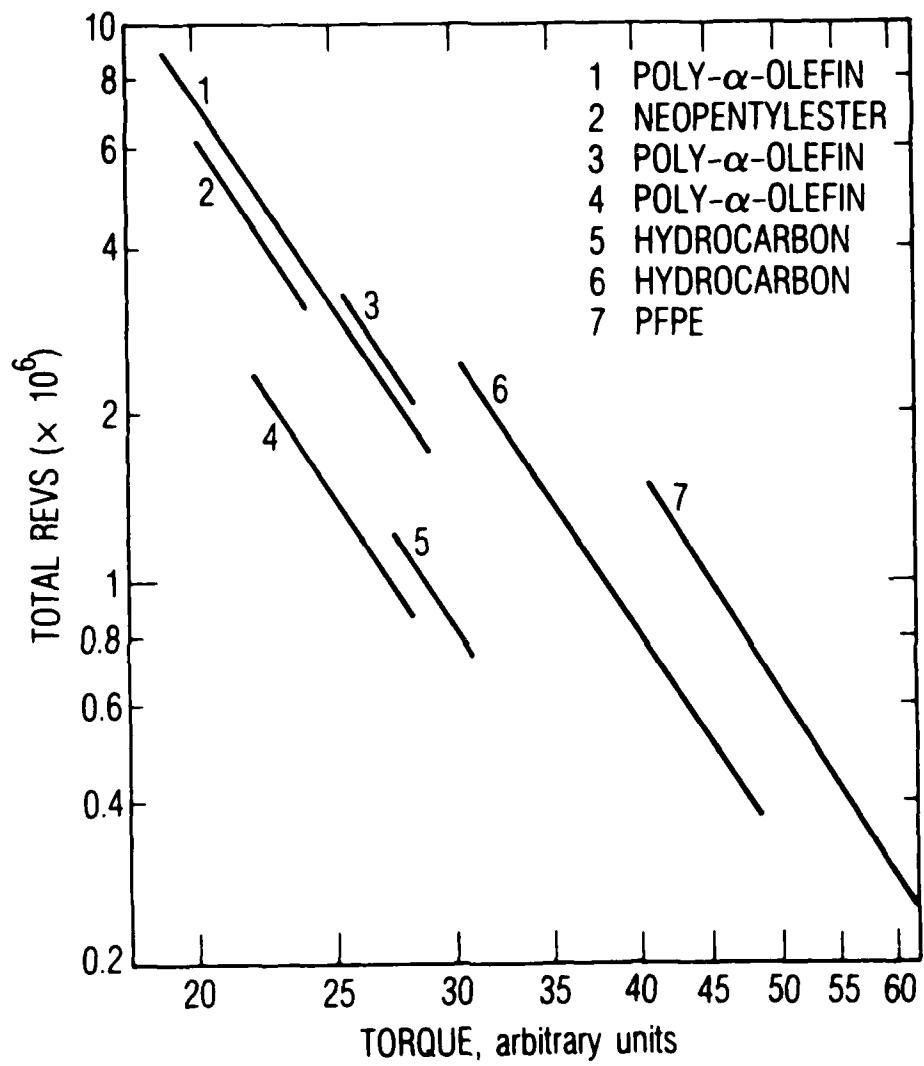


Fig. 6. Wear Life vs. Running Torque for a Series of Oils

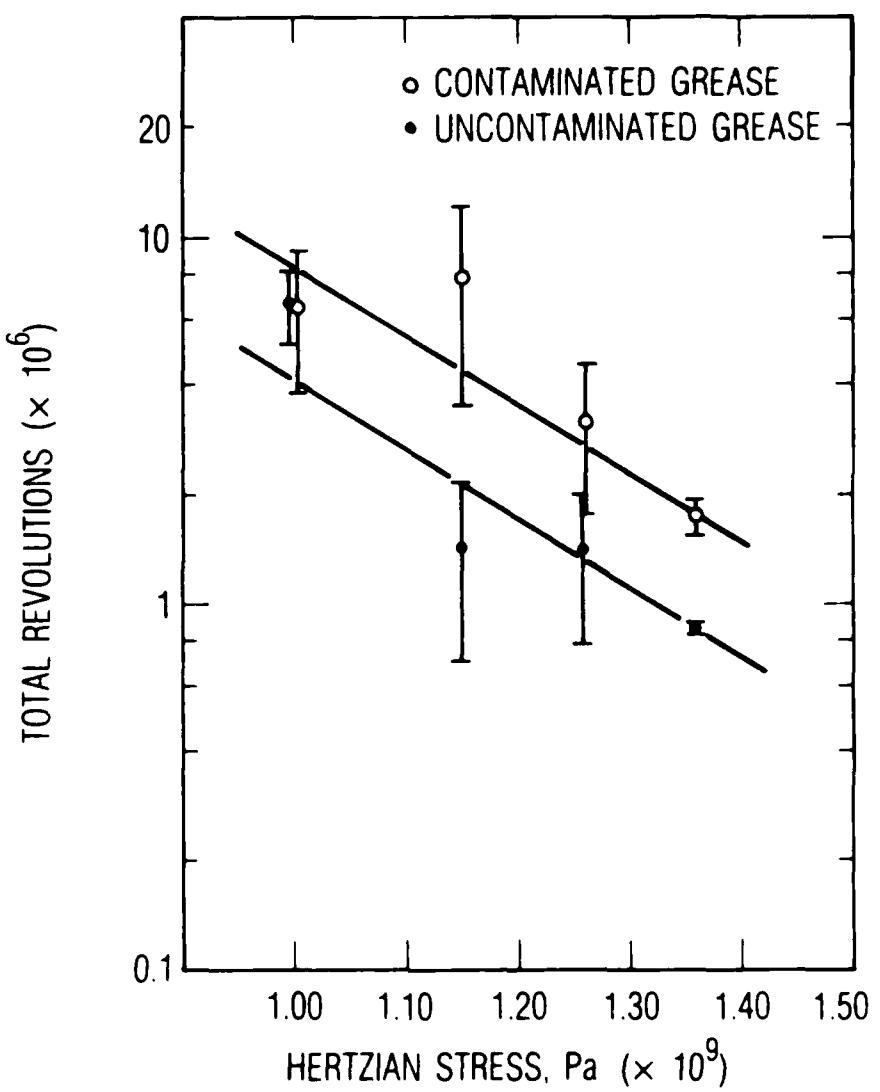
the most important aspect of the data in Fig. 6 is that the synthetic-hydrocarbon and petroleum-based hydrocarbon oils contained antiwear additives, with the exception of the neopentylester oil, sample 2. (These neopentylester compounds are suspected of forming antiwear compounds in situ, by reacting with exposed iron.) The significance of antiwear additives under boundary conditions is further supported by the data given in Fig. 7.

In these experiments the contaminant in the grease was one of the poly-alpha-olefin oils tested previously (lubricant no. 1 in Fig. 6). The results are remarkable. The contaminated grease outperformed the uncontaminated grease by a factor of 2 over a considerable range of Hertzian stresses, from 1.45 to 1.97×10^5 psi (1.00 to 1.36×10^9 Pa). In addition, the performance of the contaminated grease was comparable to the performance of the contaminant oil by itself (see Fig. 6) at the same applied load -- 30 lb (134 N) or a Hertzian stress of 1.66×10^5 psi (1.15×10^9 Pa). (The quantity of contaminant oil in the grease, 10 microliters, was the same as that used to obtain the data in Fig. 6.)

D. DEGRADATION MECHANISM

The results of the experiments discussed herein are consistent with the proposed PFPE degradation mechanism under boundary-lubrication conditions. In the absence of contaminants or other surface pretreatments, the PFPE molecules degrade by interacting with exposed metal in the contact areas. The reactions are driven by the high temperatures in the contact area which result from metal-metal asperity interactions. The implication is not that the lubricity and reactivity characteristics of the PFPE lubricants are inadequate, but rather that the material is simply unable to dissolve additives that inhibit its reaction with exposed metal. For the hydrocarbon lubricants in the boundary-lubrication regime, the antiwear additives do the work, while the function of the oil is primarily to transport the additives to the surfaces. The data in Fig. 7 support this statement.

The observation that the contaminant oil with its additives provided the antiwear protection leads to the conclusion that PFPE did not contribute significantly to the lubrication, and that its degradation was delayed because



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Fig. 7. Wear Life vs. Applied Load for Hydrocarbon-Oil-Contaminated and Uncontaminated PFPE Oil-Based Grease

the exposed metal surfaces were preferentially coated by the additives. Through the resultant "shielding" of the surfaces, the PFPE molecules were prevented from interacting with bare metal. As the antiwear additives were depleted through the wear process, the degradation of the PFPE material commenced; the result was lubricant and system failure.

If this metal-interaction hypothesis is correct, the degradation of the PFPE lubricant could be significantly reduced if one could prevent the PFPE from reacting with exposed metal. The use of ceramic (Si_3N_4) or hard-coated (TiC) bearing balls has been shown to result in significantly reduced wear and minimal lubricant degradation (for hydrocarbon lubricants) in bearing tests.¹⁹⁻²¹ Apparently the use of dissimilar materials eliminates "welding" interactions between contacting asperities, thus reducing the rate of wear and exposure of fresh metal surfaces.

Further exploration of the lubricity properties of the PFPE lubricants might allow such ceramic and hard-coated materials to be used without interference from metal-catalyzed degradation.

III. CONCLUSIONS

The results of the experiments discussed herein lead to the following major conclusions: (1) Consistent with our degradation hypothesis, PFPE fluids do not perform well under boundary-lubrication conditions under vacuum in the presence of steel components, primarily because of autocatalytic reactions with iron. (2) The surface shielding that antiwear additives normally afford hydrocarbon oils does not occur with PFPE fluids, because of the lack of sufficient additive solubility in the fluids. (3) PFPE lubricant performance under boundary conditions can only be improved through measures that prevent or substantially reduce interactions between PFPE and bare iron metal; this could possibly be accomplished by synthesizing additives that are soluble in the PFPE fluid, or by blocking the interactions via surface pretreatment or the use of dissimilar bearing materials.

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Computer Science Laboratory: Program verification, program translation, performance-sensitive system design, distributed architectures for spaceborne computers, fault-tolerant computer systems, artificial intelligence, micro-electronics applications, communication protocols, and computer security.

Electronics Research Laboratory: Microelectronics, solid-state device physics, compound semiconductors, radiation hardening; electro-optics, quantum electronics, solid-state lasers, optical propagation and communications; microwave semiconductor devices, microwave/millimeter wave measurements, diagnostics and radiometry, microwave/millimeter wave thermionic devices; atomic time and frequency standards; antennas, rf systems, electromagnetic propagation phenomena, space communication systems.

Materials Sciences Laboratory: Development of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; non-destructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures as well as in space and enemy-induced environments.

Space Sciences Laboratory: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation.